

## Effects of Thermal and Solvent Pretreatments on the Elastic Properties of Coal

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### INTRODUCTION

It is now well established that thermal pretreatment in a range of temperatures lower than those needed for pyrolysis can significantly affect the penetrability and swellability of coals. This suggests that judicious use of heat together with effective swelling solvents for coal, can affect mass transport of reagents or catalysts into or out of the coal, during the early stages of liquefaction.

The present study is concerned with the effects of heat/solvent pretreatments on the elastic constants of the coal network structure. This, in turn, tells one about how the non-covalent interactions in coal are being broken down. Studies of the elastic properties of coal are nothing new [e.g. 1-10]. Because of the compressibility of coal, the application of mercury porosimetry to pore characterization in coal has involved careful corrections, so that the actual pore size distribution could be calculated [1,11,12]. However, the limitation caused by compressibility of bulk coal structure can be an advantage in revealing the structural changes during pretreatment processes and in establishing a suitable elastic model for macromolecular coal structure.

It is known that dynamic mechanical methods are ca. 1000 times more sensitive for detecting molecular relaxations such as the glass transition temperature,  $T_g$ , than are differential scanning calorimetry (DSC)/differential thermal analysis (DTA) techniques [13]. Weller and Wert [7-10] have extensively applied the torsion pendulum technique, one of the dynamic mechanical methods, for elucidating the elastic properties of coal in the temperature range below 200 °C. They employed square rods cut from whole coal. Since the relevant temperature range for the structural relaxation by heat is generally higher than 200°C, we decided to study the thermal structural relaxation at temperatures higher than 200°C by employing dynamic mechanical analysis (DMA). This technique involves constant amplitude oscillation of the solid to determine stress-strain properties.

### EXPERIMENTAL

A DuPont 982 DMA was employed for mechanical analysis. A detailed description of the equipment has been given elsewhere [13,14]. The sample for the DMA was prepared by pressing the as-received coal powder (-100 mesh) obtained from the Argonne Premium Sample Bank with a press normally used for making FTIR sample pellets, at 15 kpsi for 6-12 hr, which results in a sample of ca. 4 mm thickness with 12.8 mm diameter.

Slippage of the samples from the clamps inside the DMA, especially during oscillation in the high temperature range (>300°C), was noted to be a main cause for irreproducibility, and special care was taken to make certain that the sample was tightly clamped. The pelletizing process used here clearly creates a solid tablet of different macroscopic mechanical properties than the original solid. The choice to work with samples prepared in this way was dictated by a desire to continue to use the Argonne Premium Coal Samples, that are generally only available in powdered form. The gross macroscopic

mechanical properties of such pellets, e.g. tensile modulus, will clearly be different from those of a sample prepared, for example, by cutting a chunk from a virgin block of coal. In fact, any samples cut directly from coal could still be subject to naturally occurring heterogeneities in the coal, and thus mechanical properties are in that case still subject to large variations, depending upon the nature of the tests. This is not important for present purposes, because our goal is not to make use of macroscopic mechanical properties. Rather, we are here only interested in changes on the molecular level that manifest themselves as changes in a particular property.

For purposes of comparison, we examined the changes revealed by DMA in the context of changes earlier noted using thermal techniques, such as DSC and solvent swelling techniques. The detailed procedures for obtaining DSC and solvent swelling results have been reported earlier [15,16].

## RESULTS AND DISCUSSION

Raw DMA results are obtained as the frequency of oscillation and the damping signal. The frequency of oscillation is directly related to an elastic modulus of the sample, whereas the energy needed to maintain constant amplitude oscillation is a measure of damping within the sample [14]. Normally, the modulus is resolved into storage and loss moduli. The storage modulus corresponds to the perfectly elastic component whereas the loss modulus represents the perfectly viscous component. The dimensionless ratio of loss/storage components is defined as the damping factor,  $\tan \delta$ .

The tensile storage modulus, in absolute value, is comparable to what might be encountered in some polymer samples. We caution against placing too much emphasis on this absolute value, because of the issues related to pressing samples from powder. Instead, it is features that are clearly visible in the  $\tan \delta$  or loss modulus spectra that are of significance. It is the changes in storage modulus  $E'$  and loss modulus  $E''$ , and their ratio,  $\tan \delta = E''/E'$  that convey significant information about microscopic change in the material being tested. Both  $E''$  and  $\tan \delta$ , for example, are used to reveal glass transitions as maxima in the spectra. Physically,  $E'$  represents the elastic energy storage capacity of the material, whereas  $E''$  represents the energy lost as heat due to dissipation. Many other transitions, in addition to a glass transition, can cause changes in  $E''$ . Thus this parameter is a sensitive indicator of a change in the ability of molecular segments to move, relative to one another. It is this property we choose to focus on here. It should be also be emphasized that in a transition, such as a glass transition, the storage modulus will normally show a slow continuous decline, whereas the loss modulus (and thus  $\tan \delta$ ) will show a distinct peak. This is what makes use of this modulus preferable for detecting transition.

In Figure 1, the first transition is seen near 60°C, for different samples of wet, as-received Pittsburgh high volatile bituminous coal. This transition is normally not visible in DSC, because it is buried beneath the water evaporation peak. The position of this peak is sensitive to the presence of moisture, as is seen from Figure 2. This behavior is typical of the effects of a "plasticizing agent" in a polymer. The molecular motions of the coal chains are enhanced at low temperatures when water is present, and internal hydrogen bonding of the coal itself is suppressed by the opportunity to hydrogen bond with a solvent (in this case, water).

The large peak that is revealed by  $\tan \delta$  above 200°C coincides with a transition shown both by DSC analysis of this coal and by a change in tetrahydrofuran (THF) swellability (see Figure 3). This transition involves an irreversible relaxation of the coal structure [16,17].

Figure 4 illustrates the behavior of Upper Freeport medium volatile bituminous coal in DMA. The tensile storage modulus exhibits a continuous decline with temperature, except for two regions of more

rapid decline in modulus. The loss modulus, and thus  $\tan \delta$ , both suggest that there is a low temperature event, again probably associated with moisture in the coal, at below 100°C. The main relaxation of structure starts to occur from 240°C, as observed in both tensile storage modulus and  $\tan \delta$ . This observation augments the DSC and solvent swelling results (see Figure 5) for the same coal, in that Upper Freeport coal showed the characteristics of a relaxed coal structure such as increased swellability in solvents and endothermic peak. In the DSC, the coal exhibited a distinct endothermic peak centered around 350°C which was started from around 310°C, whereas solvent swellability increased significantly above 250°C. It is thus confirmed by DMA that solvent swelling is a more sensitive indicator of irreversible structural relaxation than is DSC.

## CONCLUSIONS

Two bituminous coals were subjected to DMA analysis and the results were compared our earlier reported DSC and solvent swelling results. Results from different techniques appear to point to the same basic conclusions with regard to transitions, although there are subtle differences between the results of different techniques. The transition related to coal moisture is more visible in DMA and solvent swelling techniques than in DSC analysis. DMA confirms that solvent swellability is a more sensitive index of macromolecular changes than is DSC. The importance of observations made by several different techniques in order to discern transitions accurately has been noted. This study confirms the usefulness of applying different techniques simultaneously for this purpose.

We noticed that good reproducibility in DMA depends upon the reproducibility of forming pellets, in our case. A main problem was small cracks generated while the pellet was released from the press. We are further pursuing these problems in order to obtain a better description of transitions and elastic properties of coal.

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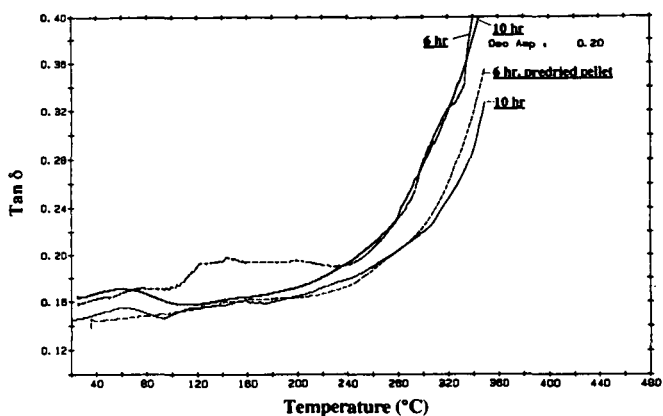


Figure 1. Tan  $\delta$  DMA spectra obtained from 4 °C/min scans of as-received and predried (up to 200°C at 4 °C/min) Pittsburgh No. 8 coal pellet samples. Pellets were made from -100 mesh powder after pressed at 15 kpsi for the duration as specified in the figure.

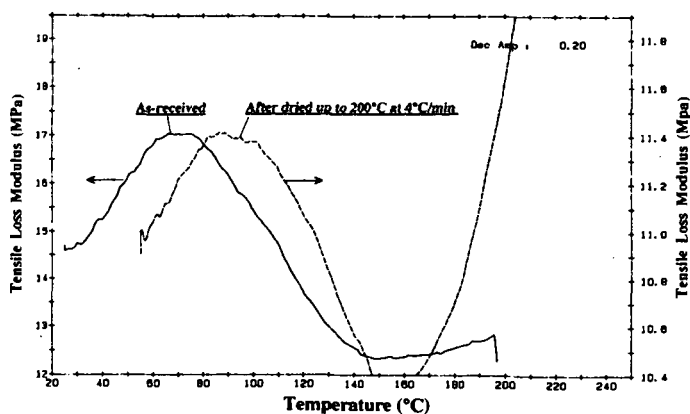


Figure 2. Effect of sample drying on tensile loss modulus obtained at 4°C/min for Pittsburgh No. 8 coal. Sample pellets were made from -100 mesh powder pressed at 15 kpsi for 10 hr.

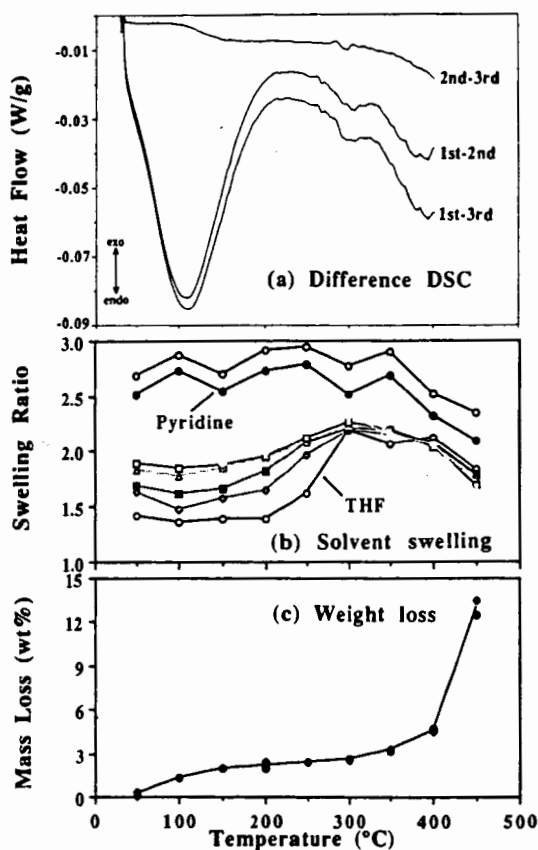


Figure 3. Difference DSC thermograms as well as profiles of solvent swelling ratio and weight loss obtained at 8 °C/min from -100 mesh Pittsburgh No. 8 coal powder (swelling time:  $\circ$ , 5 hr;  $\square$ , 1 day;  $\blacksquare$ , 2 days;  $\triangle$ , 4 days;  $\square$ , 5 days;  $\bullet$ , 6 days).

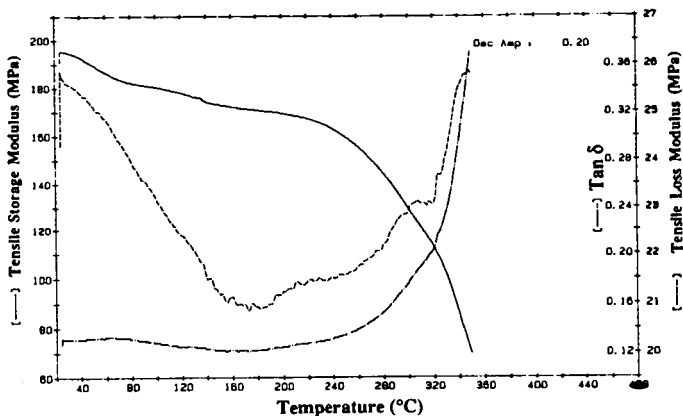


Figure 4. DMA scan of the Upper Freeport medium volatile bituminous coal obtained at 4°C/min. Sample pellet was made from -100 mesh powder pressed at 15 kpsi for 12 hr.

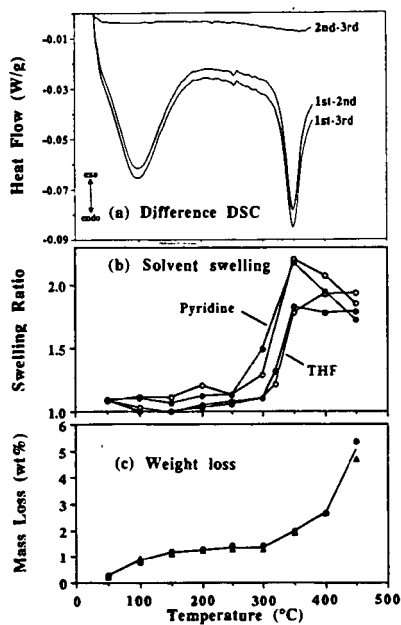


Figure 5. Difference DSC thermograms as well as profiles of solvent swelling ratio and weight loss obtained at 8°C/min from -100 mesh Upper Freeport coal powder (swelling time: 0, 5 hr; ●, 7 days).